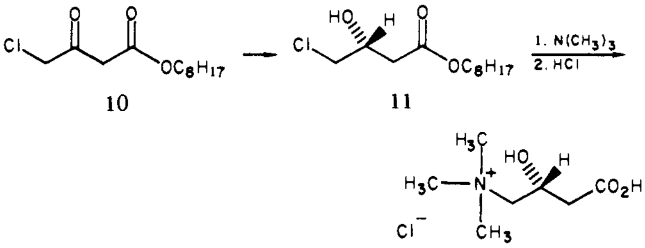
β-hydroxybutanoates of opposite configurations at different rates.

The ready availability of (R)-γ-chloro-β-hydroxybutyrate of high configurational purity allows us to complete the asymmetric synthesis of L-carnitine. This was accomplished by reaction of octyl (R)-γ-chloro-β-hydroxybutyrate (**11**) with an excess of trimethylamine in ethanol at 80 °C, followed by hydrolysis with 3 N HCl for 2 h. Crystallization from ethanol–acetone afforded L-carnitine chloride in 45% overall yield: mp 142 °C dec; $[\alpha]^{23}{}_D$ −22.9° (c 4.0, H_2O) (lit.[19] $[\alpha]_D$ −23.7°).



The feasibility of regulating the stereochemical course of yeast reduction by designing substrates with significant differences in V and/or K values for the competing enzymes provides a general method for the preparation of β-hydroxybutyric esters of either S or R configurations. Studies on the isolation and properties of the oxidoreductases are in progress.

Acknowledgment. This investigation was supported in part by grants from the University of Wisconsin Graduate School and the 3M Foundation.

Supplementary Material Available: Detailed experimental section (6 pages). Ordering information is given on any current masthead page.

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Formation of a Stable (η^2-C,C) Ketene Compound $(C_5H_5)Fe(CO)_2(CH_2CO)^+PF_6^-$ by Carbonylation of an Iron–Methylidene Complex. A Novel Entry into CO-Derived C_2 Chemistry

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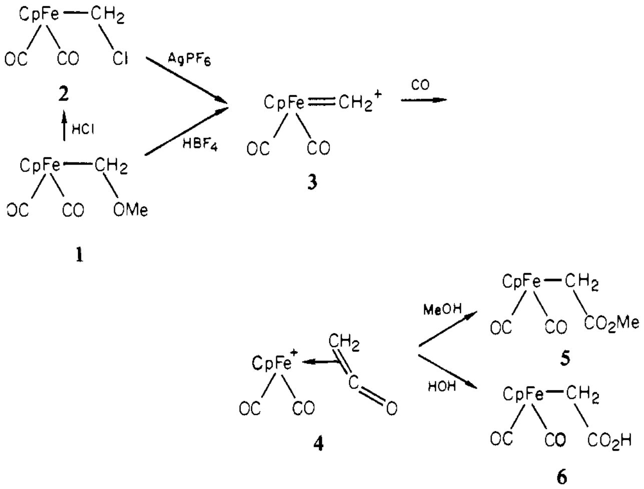
Ligated ketene obtained by carbonylating a methylidene ligand represents a plausible intermediate in homogeneous carbon monoxide fixation, and indeed postulated mechanisms for homogeneous analogues of the Fischer–Tropsch synthesis[1] sometimes incorporate μ-[η^2-C,C] ketene complexes MCH_2COM.[2] Ketenyl/carbonylmethylidene (CRCO)[3] and ketenylidene/carbonylmethylidyne (CCO)[4] ligands additionally result from transferring CO to the requisite C_1 ligand. Very little is known, however, about the carbonylation of terminal methylidene ligands,[5] although (η^2-C,O) ketene complexes of Cp_2Ti and Zr[6] have been obtained by other procedures. More is known about substituted ketenes: uncoordinated species can be generated by carbonylating their called-for carbene complexes,[7] or a number of stable diphenylketene complexes can be prepared by its direct ligation.[8] Of particular relevance to the present study is Herrmann's observation that $Cp(CO)_2Mn(CPh_2)$ converts to its stable (η^2-C,C) diphenylketene complex[9a] under CO pressure,[9b] possibly via intermolecular carbene transfer to a metal carbonyl. He found no evidence for either CO addition to the ligated carbene or the postulated carbene-CO migratory insertion[5,7a,10] in studies with the analogous anthronylketene complex.

Scheme I



We now report that (1) an electrophilic methylidene ligand picks up exogenous CO under extremely mild conditions, giving a stable (η^2-C,C) ketene complex, and (2) this ketene ligand transforms into its carbomethoxymethyl group, representing a novel synthesis of a C_2 alkyl ligand from carbon monoxide.

The extremely reactive methylidene salt $FpCH_2^+PF_6^-$ (**3**),[11] Fp = $Cp(CO)_2Fe$, affords the known carbomethoxymethyl

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[†] Work initiated at Wesleyan University, Department of Chemistry, Middletown, CT 06457.

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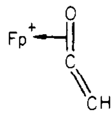
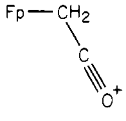
$FpCH_2CO_2Me$ (**5**)[12] via a carbonylation/methanolysis sequence (Scheme I). Thus treatment of a CH_2Cl solution (−80 °C) of $FpCH_2Cl$ (**2**) with $AgPF_6$ under 1 atm of CO was followed by immediate pressurization (85 psig CO), warming to 25 °C (0.5 h), venting of pressure, and quenching with methanol Et_3N (1.5 equiv). Column chromatography of CH_2Cl_2 extracts produced **5** (93%), while subsequent CH_3NO_2 extraction of the residue and ether precipitation left 3% each of $FpCO^+$ and $Fp(CH_2CH_2)^+$. Only slightly diminished yields of **5** result upon using just 1 atm of CO (1 h) and quenching either with methanol then Et_3N (81% yield) or with 1 equiv of $PhCH_2(Me)_3N^+OMe^-$ in methanol (85%). Using two variants of this 1-atm carbonylation procedure, we converted **2** to the carboxylic acid **6** (88%) after an aqueous workup, and we substituted acid treatment (2 equiv of $HBF_4 \cdot OEt_2$) of $FpCH_2OMe$ (**1**) in the synthesis of **5** (55%).

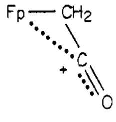
Ketene complex **4** can be isolated as a stable solid at room temperature—provided that its extreme moisture sensitivity and its insolubility or reactivity toward most organic solvents is recognized. The precipitate from the $FpCH_2Cl/AgPF_6/CO$ (85 psig) reaction needs only extraction with *dry* CH_3NO_2 and treatment of the centrifugate with CH_2Cl_2 to precipitate **4** (typically 200 mg, 48%) as a yellow solid contaminated by only 3–7% $FpCO^+$. Although CH_3NO_2 solutions of **4** remain intact for at least 8 h (25 °C), they quantitatively convert to either a mixture of **5** and $FpCH_2C(OH)OMe^+$[12b] or **6** upon addition of methanol or water, respectively. Spectral data of **4**[13] are in accord with the (η^2-C,C) ketene formulation: IR (CH_3NO_2) 2061, 2018 ($C{\equiv}O$), 2179 ($C{=}O$), (Nujol) 2060, 2018 ($C{\equiv}O$), 2168 ($C{=}O$) cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.37 (s, 5, Cp), 2.08 (s, 2, CH_2); ^{13}C NMR (gated decoupled) (CH_3NO_2) δ 210.5 (s, CO), 87.2 (d quint, Cp), 169.0 (t, ^2J = 4 Hz, $C{=}O$), −40.8 (t, $^1J_{C-H}$ = 160 Hz, CH_2).



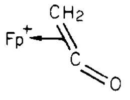
A



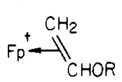
B



C



D



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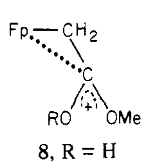
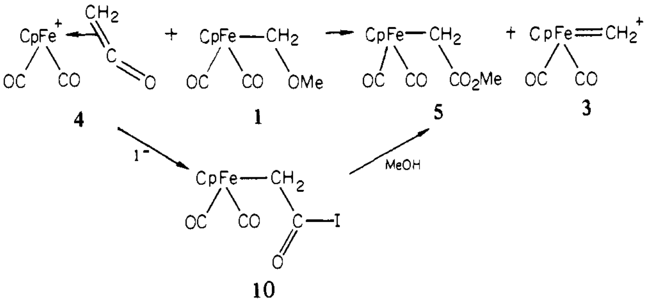


8, R = H
9, R = Et

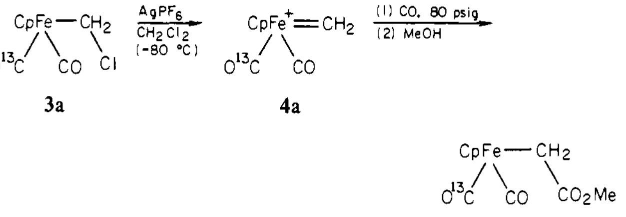
Further analysis of this spectral data moreover supports an unsymmetrically bound (η^2-C,C) structure D for **4**. An (η^2-C,O) formulation A, in contrast, would be inconsistent with the appearance of a CH_2 singlet in the ^1H NMR and of the intense IR $\nu(C{=}O)$.[6,14] Completely or even "substantially" open β-acylium structures B and C, respectively, are ruled out principally by two spectroscopic arguments. First, the ^1H NMR and IR data of **4** fit the observed linear correlation between δ Cp and $\nu(C{\equiv}O)$ for Fp complexes:[12b] **4** closely resembles the unsymmetrical[15] η^2-vinyl ether salt **7** (δ 5.52 ppm; ν(CO) 2068, 2024 cm^{-1}) rather then the β-metallacarbenium ion complex **9** (δ 5.21; ν(CO) 2040, 1990 cm^{-1}). Enough positive charge therefore resides on the Fe center of **4** to be consistent with (η^2-C,C) ketene ligation D. Second, the $^1J_{C-H}$ values, an effective probe of the s character of the carbon hybrid orbital making up the C–H bond,[16] obtained from the gated decoupled ^{13}C NMR spectra for the α-CH_2 groups on **5** (^1J = 141 Hz), **9** (^1J = 148 Hz), **4** (^1J = 160 Hz), **7** (^1J = 163 Hz), and $Fp(CH_2{=}CH_2)^+$ (^1J = 167 Hz) again disclose analogous bonding descriptions of **4** and **7**. Considerable localization of positive charge, however, must be on the ketene carbonyl C of **4** to account for its high reactivity toward nucleophiles.

Scheme II



The ketene complex **4** regioselectively adds nucleophiles at the ketene carbonyl, as evidenced by the transformation of **4** to **5** under conditions that the methoxyacetyl regioisomer $FpCOCH_2OMe$[12b] if formed is stable. Quantitative conversion of **4** to **5** also results with **1** as the methoxide donor. Attempts at making this reaction autocatalytic in **4** for converting **1** to **5** under CO pressure have, thus far, proved unsuccessful (Scheme II). Iodide also adds to **4** in a CH_2Cl_2 slurry (25 °C) and exclusively generates an unstable acyl iodide complex **10** [IR 2022, 1977 ($C{\equiv}O$), 1754 ($C{=}O$) cm^{-1}], which readily solvolyzes to **5** or **6**.

So how does the methylidene complex **2** form its ketene derivative **4**? The carbenoid center could either pick up exogenous CO, or it could migrate to a metal carbonyl—two mechanistic alternatives that we were able to discern between after doing a ^{13}C-labeling study. Treatment of $FpCH_2Cl$ containing a ^{13}C-labeled terminal carbonyl (**3a**, 51% ^{13}C labeled) with $AgFP_6$ in CH_2Cl_2 (−80 °C), then 80 psig of CO (−80 °C), and a methanol quench (20 °C) affords the carbomethoxymethyl complex **5a** (27% yield after column chromatography) with all of the ^{13}C label retained in terminal carbonyls.[17] In retrospect, proclivity of the methylidene ligand on **3** (a metallacarbenium ion species) to abstract exogenous CO resembles the established reactivity of organic carbenium ions with CO (e.g., the Koch process[19]), giving the homologous carboxylic acid after hydrolysis and the established cyclopropanating ability of **3**[11a] and related Fp alkylidene$^+$ salts[20] with olefins.



5a

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(13) Our ^1H NMR data for **4** matches that recorded by Aumann and Wörmann after dissolving **6** in HSO_3F-SO_2ClF; using only this information, they assigned structures for **4** and for $FpCH_2CH(OH)_2^+$: Aumann, R.; Wörman, H. *Chem. Ber.* **1979**, *112*, 1233.

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(17) $FpCH_3$ containing a ^{13}C-labeled terminal carbonyl[18] was converted into $FpCH_2Cl$ **3a** by the four-step sequence of iodination in CH_2Cl_2, Na(Hg) reduction in THF, alkylation with $ClCH_2OMe$, and reaction with HCl(g) in hexane (47% overall yield). Label assay was by mass spectrometry and quantitative IR.

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Carboalkoxymethyl ligands thus represent kinetically viable intermediates in the reductive coupling of two carbonyls. The first CO is secured by reducing FpCO$^+$, for example, to FpCH$_2$OMe (**1**).[21a] The second CO is incorporated as a carboalkoxymethyl ligand either by an alkyl–CO migratory insertion on **1**, followed by protic isomerization of the methoxyacetyl intermediate,[21b] or by the methylidene carbonylation route using **1** reported here.

Acknowledgment. support from the Department of Energy, Office of Basic Energy Service, is gratefully acknowledged.

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Measurement of the Rotational Barrier of a Tetraalkylhydrazine Radical Cation

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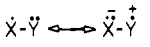
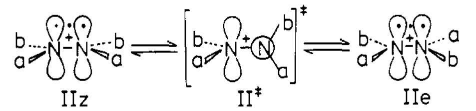
Heteroatom-substituted radicals are resonance stabilized by donation of a lone-pair electron to the radical center, as symbolized in Ia,b. The bonding involved is a three-electron bond in the


$\dot{X}\text{-}\ddot{Y} \longleftrightarrow \overset{-}{\ddot{X}}\text{-}\overset{+}{\dot{Y}}$

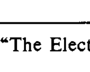
Ia Ib

Linnett[1] sense; in MO terms the odd electron is in the antibonding combination of the p orbitals at X and Y, assuming the pure p orbitals are involved. Resonance stabilization should be maximized when the atomic orbital energies of X and Y are the same[2] and when the radical is charged.[3] Hydrazine radical cations should be among the most stable compounds with three-electron π bonds. The strength of the three-electron π bond of hydrazine radical cations is thus of interest in assessing the degree of stabilization of a radical center by a heteroatom. As indicated in IIz $\rightleftarrows$ IIe,

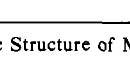


IIz II‡ IIe

rotation about the three-electron π bond of a hydrazine radical cation leads to a loss of resonance stabilization when the orbital axes are perpendicular (at the transition state for rotation (II‡)). We report here the measurement of the barrier to rotation in a tetraalkylhydrazine radical. It was previously shown that 9,9′-bi(9-azabicyclo[3.3.1]nonane) (**1**) gives an isolable, Bredt's Rule protected radical cation and has an electrochemically reversible second oxidation to **1**$^{2+}$.[4] 8,8′-Bi(8-azabicyclo[3.2.1]octane) (**2**)

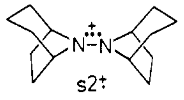


1

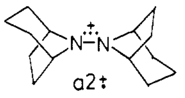


2

has similar kinetic protection and also lower symmetry, so that 180° rotation about the NN bond interconverts syn and anti isomers. The CV curve of **2** shows a single reversible first oxidation wave (E°_1 = 0.13 V), but two reversible second oxidation waves ($E^\circ_2{}'$ = 1.02, 1.14 V).[5] The relative sizes of the second-oxidation waves are scan-rate dependent, the 1.02-V wave being small at slow scan rates but growing until it is about as large as the 1.14-V wave at fast scan rates. This behavior suggests that the isomeric radical cations **s2**$^{+\cdot}$ and **a2**$^{+\cdot}$ oxidize to their respective dications

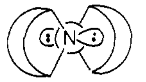


s2$^{+\cdot}$

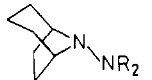


a2$^{+\cdot}$

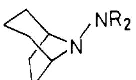
at different potentials and that they interconvert during slow scans. The reason for the nearly equal sizes of the two second oxidation waves at fast scan rates was revealed by low-temperature ^{13}C NMR study of neutral **2**. As does **1**,[4] **2** exists only in the electronically destabilized lone pair, lone pair dihedral angle θ = 180° conformations shown in Newman projection along the NN bond as III, because of the steric demands of the substituents. At each



III



2E



2A

bicyclic ring, the NR$_2$ substituent can be equatorial (**2E**) or axial (**2A**) to the piperidine fragment, so neutral **2** exists in three conformations of different energy, **2EE**; **2EA**/**2AE**; and **2AA**. Both NN rotation and N inversion are frozen out on the NMR timescale at low temperature, and all three conformations are present at equilibrium. Integration of the ^{13}C NMR at −75 °C was consistent with **2EE** being stabler, **2EA**/**2AE** being 0.2$_4$ kcal/mol higher in free energy, and **2AA** being an additional 0.2$_4$ kcal/mol higher in energy. Because electron removal from both **2EE** and **2AA** without NN rotation gives **a2**$^{+\cdot}$ and from **2EA**/**2AE** gives **s2**$^{+\cdot}$, the NMR work predicts a ratio of 0.86 for **s2**$^{+\cdot}$/**a2**$^{+\cdot}$ at the fast scan-rate limit (assuming no solvent effect on the equilibrium and that $\Delta S^\circ = 0$), in excellent agreement with the experimental observation of about equal sizes for the 1.02 and 1.14 V second-oxidation waves.

The difference in $E^\circ_2{}'$, corresponding to oxidation of the isomers of **2**$^{+\cdot}$ to those of **2**$^{2+}$, is 0.12 V, corresponding to a 2.8-kcal/mol difference in ease of second-electron removal. A large $\Delta E^\circ_2{}'$ is crucial for analysis of the isomeric mixture. We would not have predicted a large difference. We would have expected an energy difference for either **2**$^{+\cdot}$ or **2**$^{2+}$ similar to that for the corresponding hydrocarbons, *syn*- and *anti*-bi(bicyclo[3.2.1]oct-8-ylidine), for which Allinger's MM2 program[6] predicts only a 0.1-kcal/mol difference, with the syn form being the least stable.

Oxidation of **2** with NOPF$_6$ gives **2**$^+$PF$_6^-$ as a yellow solid, which was crystallized from acetone to analytical purity. Solutions of this solid in acetonitrile gave a UV spectrum having λ_m 334 nm (ϵ 2100), and ESR parameters of $g = 2.0033$ and $a(2\text{N}) = 13.7$ G and complex proton splitting patterns with a major line separation of about 4 G. When the solid is dissolved at −30 °C,

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(3) Clark, T. *J. Comput. Chem.* **1981**, *2*, 261; *Ibid.*, in press.

(4) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392. (b) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *Ibid.* **1978**, *100*, 7876.

(5) (a) All CV data are reported for 1–2 mM solutions in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, with a planar gold working electrode and a saturated calomel reference electrode. (b) The first oxidation wave resolves into two observed waves at low temperature. The **2**,**2**$^+$ wave is complicated by the fact that *syn*- and *anti*-**2**$^+$ can interconvert without undergoing rotation about the three-electron π bond by the following electron transfer:

$$(\text{syn})^0 + (\text{anti})^+ \rightleftarrows (\text{syn})^+ + (\text{anti})^0$$

This electron transfer is remarkably slow, and will be discussed, along with the scan rate and temperature dependence of the **2**,**2**$^+$ oxidation wave, in a later publication.

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127; Program No. 395, QCPE, Indiana University, Bloomington, IN.

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